Functionalization of Carbon Nanotubes Using Atomic Hydrogen

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ABSTRACT

We have investigated the irradiation of multi walled and single walled carbon nanotubes (SWNTs) with atomic hydrogen. After irradiating the SWNT sample, a band at 2940 cm^{-1} (3.4 μm) that is characteristic of the C-H stretching mode is observed using Fourier transform infrared (FTIR) spectroscopy. Additional confirmation of SWNT functionalization is tested by irradiating with atomic deuterium. A weak band in the region 1940 cm^{-1} (5.2 μm) to 2450 cm^{-1} (4.1 μm) corresponding to C-D stretching mode is also observed in the FTIR spectrum. This technique provides a clean gas phase process for the functionalization of SWNTs, which could lead to further chemical manipulation and/or the tuning of the electronic properties of SWNTs for nanodevice applications.

Single-walled carbon nanotubes (SWNTs) have been considered as single molecular units for nanoelectronic devices, possible sorbents for hydrogen fuel storage, and in numerous other applications[1]. In order to realize many of these applications, chemical processing methods need to be developed that allow for the direct manipulation and tuning of the chemical and physical properties. Gas phase functionalization techniques could prove extremely useful to fabricate sensors and devices based on SWNTs[2,3]. One of the challenges in fabricating large arrays of SWNT devices is the lack of selectivity in obtaining SWNTs with the desired electronic properties. There-fore, there is a need for developing methods for the post-growth manipulation of the electrical transport properties of the nanotubes. For instance, introduction of C-H bonds in metallic SWNTs will introduce barriers to electron transport that may lead to useful semiconducting devices[4]. Also, hydrogenated nanotubes may impart radiation shielding properties to composites for space applications. Here we describe a clean gas phase process for the functionalization of SWNTs producing a C-H bond.

Previous work on multiwall carbon nanotubes (MWNTs) has shown one broad asymmetric line at 1575 cm^{-1} and a weaker line at 868 cm^{-1} in the transmission infrared spectrum. Kuhlmann et al. reported[5] weak IR

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absorptions at 1598 ± 3 cm^{-1} and 874 ± 2 cm^{-1} in SWNT and 1590 cm^{-1} and 868 cm^{-1} in polycrystalline graphite samples. The intensity of the band at 868 cm^{-1} is ~0.015 absorbance unit or 96.6% transmission. Since many of these bands are weak, care must be taken to ensure that the collection of the spectrum is not masked by background interferences[6]. Kastner et al.[7] were able to observe the weak band at 1575 cm^{-1} because they obtained their spectrum using a vacuum spectrometer where the background absorption due to water vapor is eliminated.

There have been limited reports of the direct functionalization[8,9] of SWNTs. One of the inherent difficulties is the challenge presented in purifying and handling the SWNTs. Recently Koshio et al. reacted SWNTs with monochlorobenzene (MCB) or poly (methyl methacrylate) (PMMA) by subjecting SWNTs to ultrasonication[10]. In the latter case, SWNTs were dispersed in a 2 % solution of PMMA in MCB. FTIR spectra for SWNT/MCB mixture produced peaks at 2848 and 2920 cm^{-1} corresponding to the stretching mode of C-H bond vibration in saturated hydrocarbons. For the SWNT/PMMA/MCB mixture, they found two additional peaks at 2949 and 2989 cm^{-1} suggesting that two different species produced by the decomposition of PMMA reacted with the reactive sites induced on SWNTs by ultrasound. They also found a band at 1729 cm^{-1} due to C=O bond in carbonyl groups that arises from the presence of dissolved oxygen in the solvent. Recently Chen et al. used plasma chemical modification of CNTs and subsequent reactions exploiting plasma induced surface functionalities[11].

Our attempts to functionalize carbon nanotubes (CNTs) use a cold plasma enhanced gas phase approach. In the cold plasma, the gas flow is maintained at a fraction of a Torr pressure in the plasma chamber. The energy is supplied to the flowing gas by a radiofrequency (RF) generator designed to provide up to 100 Watts of continuous wave (13.56 MHz) power to the reaction chamber. Maximum power transfer from the RF amplifier tubes to the reaction chamber is accomplished by matching the output impedance of the generator to the input impedance of the reaction chamber. A glow discharge with characteristic high electron energies is produced in the reaction chamber. The temperature of the gas is typically ~1000 K (0.05 - 0.1 eV), which is much lower than that of the electrons at a few eVs. The glow discharge produces electrons by ionization and radicals by bond dissociation, thus providing the atomic hydrogen for functionalization. The plasma may also introduce defects in CNTs which will serve to reduce the activation energy for chemisorption.

Our initial experiments employed CVD-grown MWNTs deposited on an iridium-coated silicon wafer[12]. No spectral features were found above the background of the FTIR spectrometer. A Thermo Nicolet Nexus 670 FTIR spectrometer was employed in our investigations. Reaction of hydrogen plasma with MWNTs was carried out for 45 minutes and a small IR signal above the background in the C-H stretch region is barely indicated (Figure 1). Further plasma processing for a total of 135 minutes resulted in no significant change in the IR band due to limited penetration depth of the charged particles. The penetration depth of electrons with energy 10 eV is only 10 – 20 nm. Furthermore, the H atom may possess much less energy and will therefore

barely process the outer layers of the MWNTs. This may be the reason why the intensity of the C-H band does not increase regardless of how long MWNTs are irradiated by H atoms in the plasma chamber. Additionally, since only the outer most layer is available for functionalization, the total accessible C for functionalization is very low compared to the total amount of C in the MWNTs.

It is important to note that while the H_2 plasma is on, CNTs are exposed to harmful vacuum UV radiation (Lyman-α) produced in the plasma that can dissociate some of the C-H bonds as they are formed. Since we have no control over the penetration depth of the H atoms or the amount of UV radiation in this experimental set-up, we designed a new apparatus to eliminate exposure of the CNT sample to UV radiation while permitting H atoms to constantly impinge on the sample. This setup and the results will be described further in detail shortly.

It is known that UV irradiation decreases the intensity of the C-H stretching feature in hydrogenated carbon materials[13-15] and therefore it is important to ensure that the rate of C-H bond formation is higher than the rate of destruction of the C-H bond by the UV radiation. Mennella et al. have removed the UV radiation and shown that C-H modes are activated in nano-sized hydrogen-free carbon particles by exposure to atomic hydrogen[16]. We have adopted this approach for formation of C-H bonds in SWNTs.

Based on Mennella's work[16], we wanted to eliminate the UV component of the discharge. The application of microwave and radio frequency excited discharge sources for the production of intense beams of atomic, radical, and metastable species is well established. They have extensively been adopted for experiments with atomic hydrogen in several research fields. A schematic of our apparatus is shown in Figure 2. The source used in our experiment consists of a Pyrex tube with an inner diameter of 10 mm and 1 mm thickness inserted in an McCarroll cavity operated at 2.45 GHz. Microwave power is supplied by an Opthos microwave generator (model MPG 4M). The input wattage for the microwave generator was 45 Watts and the reflected power was at ~ 8 Watts. The exit end of the tube is connected to a vacuum chamber (in which the sample is located) through a Teflon plug with a 1 mm bore down the center that collimates the H atom stream toward the target. This aperture allows the buildup of gas needed for a localized discharge[17]. To prevent UV radiation produced in the discharge region from hitting the sample, the entrance hole of the Teflon plug is designed off-axis, which allows only H atoms to pass.

We used a special glass cryostat where a calcium fluoride window coated with purified SWNTs is fastened in the center of the cryostat that is on the end of a Dewar container that can be filled with liquid nitrogen. However, all of our functionalization studies were carried out at room temperature. The sample can be rotated to any position as the bottom shroud with two CaF_2 windows is fixed and the top cryostat and the shroud are connected by a ground glass joint (Figure 2). This allows for recording of the spectra during the irradiation process in order to monitor the progress of functionalization. The bottom shroud has two openings; one connected to the H atom source and one across connected to the high vacuum pumping system. At 90° to these openings, the shroud is

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equipped with two CaF_2 windows capable of permitting an IR beam to pass through the sample for taking the spectrum. Before we started the irradiation, we took a spectrum of the SWNT that served as the background.

The pressure of H_2 gas at the entrance of the UV lamp was maintained at 500 μm Hg, while the pressure at the exit of the shroud read about 1 μm Hg. Since the pressure difference is 500 μm to 1 μm, there is a beam of H atoms hitting the SWNTs on CaF_2 substrate. HiPCO derived SWNT samples provided by Rice University[18] were used in this study. Purification of the SWNTs was carried out by transferring 50 mg of the sample to a 50 ml flask with the addition of 25 ml of concentrated HCl and 10 ml of concentrated HNO_3. The solution was heated for 3 hours and constantly stirred with a magnetic stirrer in a reflux apparatus equipped with a water-cooled condenser. This was done to remove the unwanted iron/graphite nanocrystallites that are a by-product of the production process. The resulting suspension was then transferred into centrifuge tubes and spun-down at 3220 g for 30 minutes. After pouring off the supernatant, the solid was resuspended and spun-down (30 min) three times in deionized water. Next, the solid was treated with NaOH (0.01 M) and centrifuged for 30 minutes. We qualitatively confirmed the purity of the SWNTs before and after purification using transmission electron microscopy (data not shown here). As evidenced by TEM, removal of the Fe nanoparticles was accomplished, and the crystallinity of the SWNTs was maintained. Finally, the sample was dried using a vacuum oven kept at 60° C overnight. The SWNTs were then suspended in CCl_4 in

order to deposit a film of SWNTs on the calcium fluoride windows.

Figure 3 clearly demonstrates that the C-H bonds are formed. The important result is that H atom irradiation on SWNTs produced a band at 2940 cm^{-1} (3.4 μm) with subfeatures at 2949, 2918, and 2848 cm^{-1} typical of the C-H stretching vibrations in CH_2 and CH_3 groups. There is no evidence for aromatic C-H modes (~3040 cm^{-1}). We are not able to see the corresponding bending mode because it is obscured by a strong water band from the background of the spectrometer. It is noted that the intensity of the peaks in Fig. 3 does not change regardless of the irradiation time from 1 to 7 hours. Future controlled experiments will determine the minimum irridation time required for functionalization and extent of hydrogen coverage as these are all issues of importance in applications. To confirm C-H stretching mode in SWNTs, we functionalized with D atoms by replacing hydrogen gas with deuterium in the microwave discharge. A weak band in the region 1940 cm^{-1} (5.2 μm) to 2450 cm^{-1} (4.1 μm) corresponding to C-D stretching mode is observed in the FTIR spectrum. However, the background spectrum of air (CO_2 and H_2O) in the spectrometer combined with the limited signal intensity prevents us from confirming this band. We are currently developing the use of a vacuum FTIR spectrometer so we have no subtraction problem of the CO_2 and H_2O bands.

Direct hydrogenation of SWNT has been studied by quantum chemistry and other theoretical methods[19] with the conclusion that the addition of molecular hydrogen to nanotube is a slightly exothermic process. Atomic hydrogen can chemisorb on CNT sidewalls with a

binding energy of ~26 kcal/mol[20]. The chemisorption and desorption energies of H on CNT, however, depend on the coverage of H on the nanotube. At low coverages, the binding energy of an isolated H might be little lower than when other H atoms start to chemisorb on the neighboring sites. At very high coverages however, H atoms from the neighboring sites could spontaneously desorb as H_2 molecules. We expect, therefore, the system to be in a dynamic equilibrium at an intermediate coverage between the above two limits. The H chemisorption coverage and the FTIR line shapes and positions will not change much after that limiting coverage has been achieved. An indication of the above scenario is that in the experiments we do not observe any change in the spectra when the exposure time is increased from about 30 minutes to few hours. More accurate time resolved data, in future, for exposure times much shorter than 30 minutes may help to verify the above explanation. Based on mechanisms proposed by Kuznetsova et al[1], it is likely that plasma processing of the SWNT sample creates openings in the sidewalls with dangling –C=C groups which are susceptible to hydrogenation. In this manner the functionalized nanotubes probably have short alkyl groups attached to the sidewalls at these openings. However, there is no clear evidence for such substitution reaction here.

In conclusion, we have successfully functionalized SWNTs using hydrogen atoms from a microwave discharge. A key parameter was the elimination of the UV component from the discharge. This clean and simple technique has the advantage of giving very clear results compared to wet chemical reactions which can produce polymeric material that produce noise in the transmission spectra. The approach can be used to functionalize nanotubes with other species such as N, F, NH, etc.

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mode of the water molecule in our spectrometer. After purging the spectrometer with dry air and subtracting the residual water remaining after purging, it is difficult to justify its presence with certainty because to start with, this IR active CNT band is also a weak line (0.02 absorbance unit or 95% transmission).

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Figure Captions:

Figure 1. FTIR spectra of MWNTs after processing with cold hydrogen plasma. C-H stretch above the noise level is indicated. Curve (a) is after 45 min irradiation and curve (b) is after 135 min.

Figure 2. Apparatus to irradiate SWNTs by H atoms produced in a microwave discharge. H atoms enter through two 1 mm holes (a) in a Teflon plug at 90° to the target. This hole is joined by another 1 mm hole (b) through the center of the plug directing the H atoms in a beam to the target.

Figure 3. FTIR spectra of SWNTs irradiated by H-atoms. C-H bands at 2949, 2918, and 2848 cm^{-1} are clearly indicated.
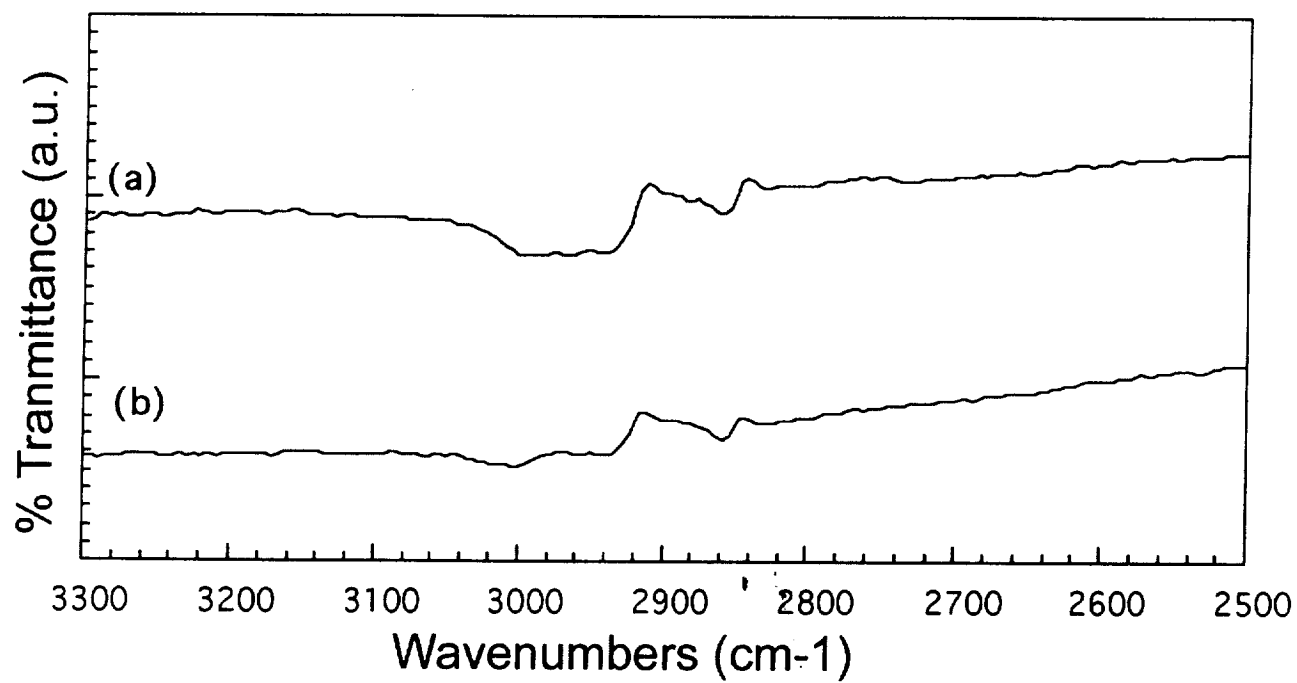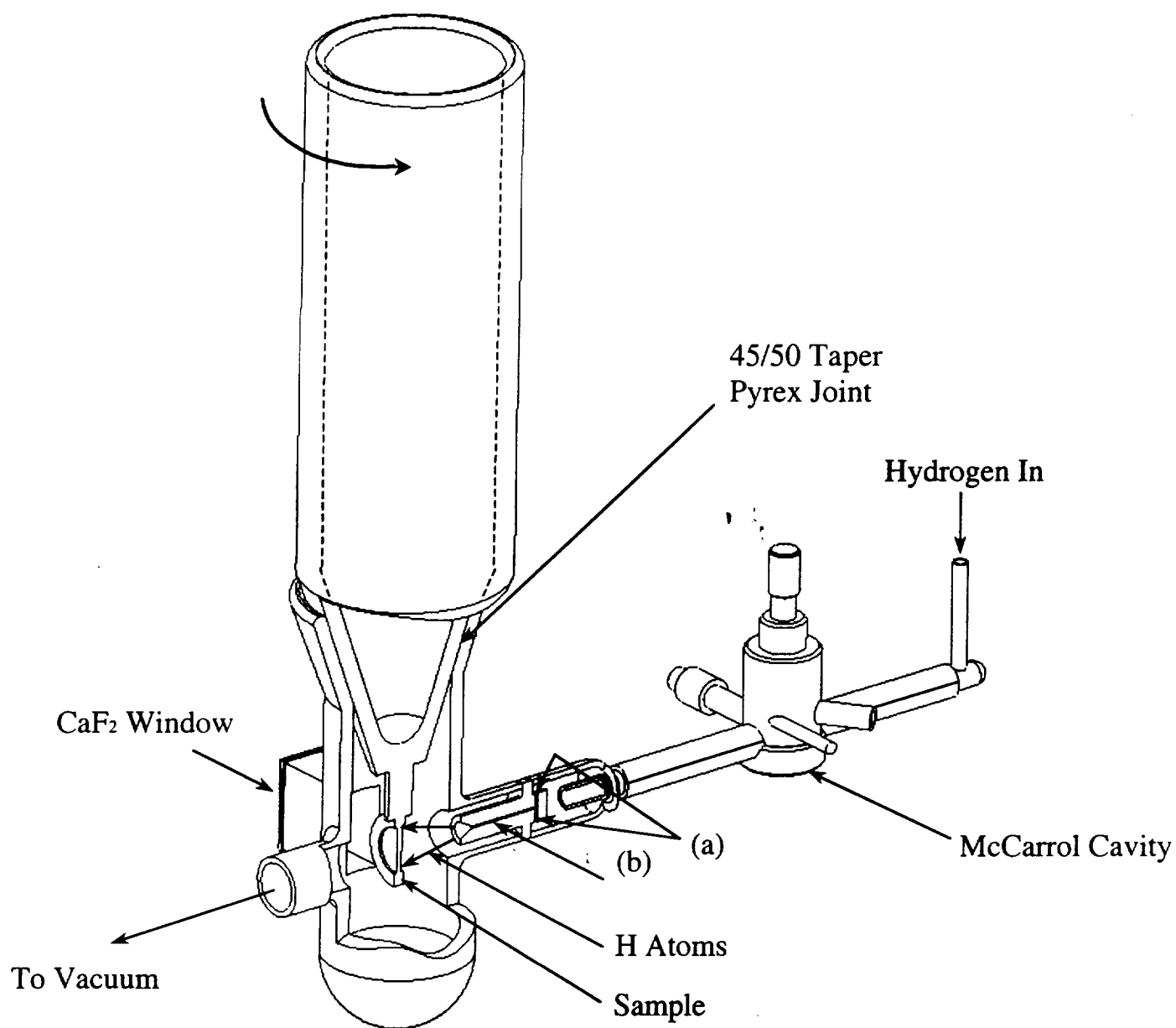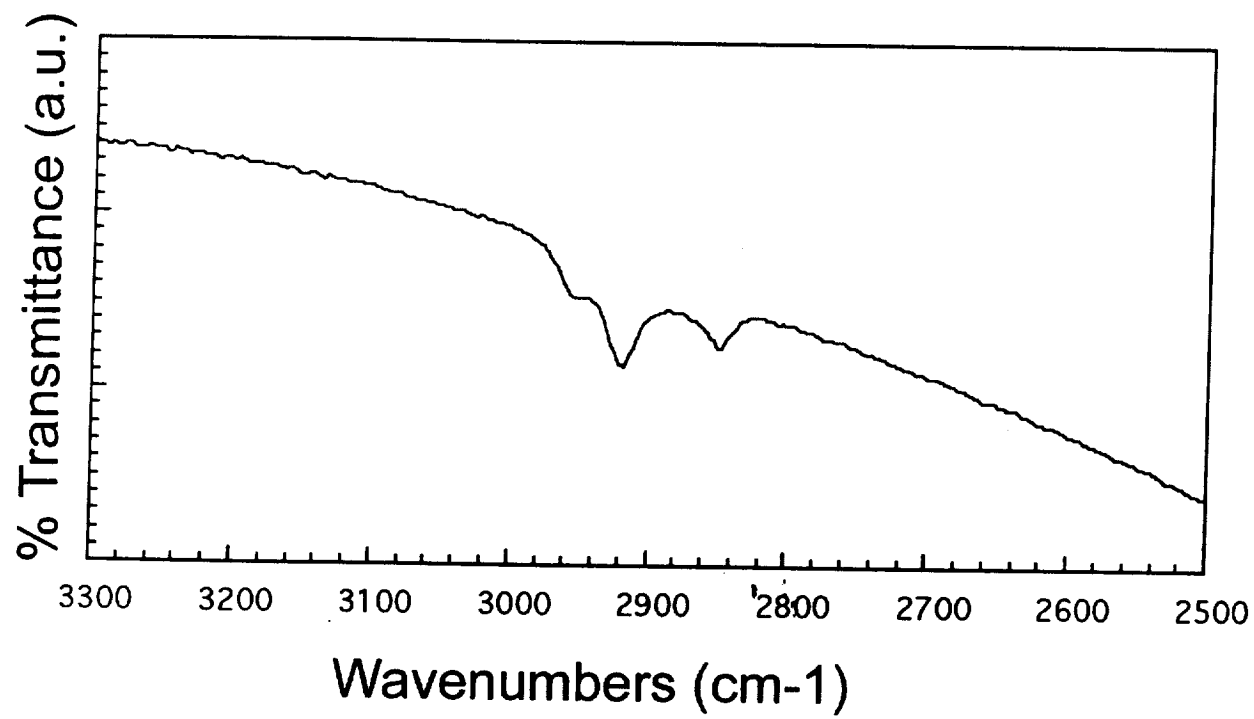
Figure 1.

45/50 Taper
Pyrex Joint

Hydrogen In

CaF₂ Window

McCarrol Cavity

(a)

(b)

H Atoms

Sample

To Vacuum

Figure 2.

Figure 3.